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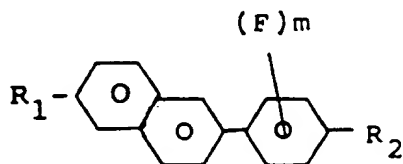
(52) UK CL (Edition K)
C2C CAA CMB CNR CWR C202 C22Y C220 C222
C226 C227 C30Y C31Y C311 C326 C36Y C364
C43X C62Y C624 C662 C666 C68Y C694 C697
C80Y C821
C4X X12
U1S S1387

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2526 (& Chem. Abstr. 84:164566z)
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 CWR
 INT CL⁵ C07C
 Online databases : CAS ONLINE

(54) **Liquid crystalline phenyl-naphthalenes**

(57) Novel phenyl-naphthalenes having liquid crystalline properties are disclosed of general formula I:



Formula I

wherein R₁ is C₁₋₁₅ alkyl or alkoxy or perfluoroalkyl or perfluoroalkoxy or CN; R₂ is CN, halogen, C₁₋₁₅ perfluoroalkyl or perfluoroalkoxy, NCS, C₁₋₁₅ alkyl or alkynyl or alkoxy; m is 0, 1 or 2; provided that R₁ and R₂ are not both alkyl, alkoxy, perfluoroalkyl or perfluoroalkoxy unless m is 0.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1990.

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Fig. 1.

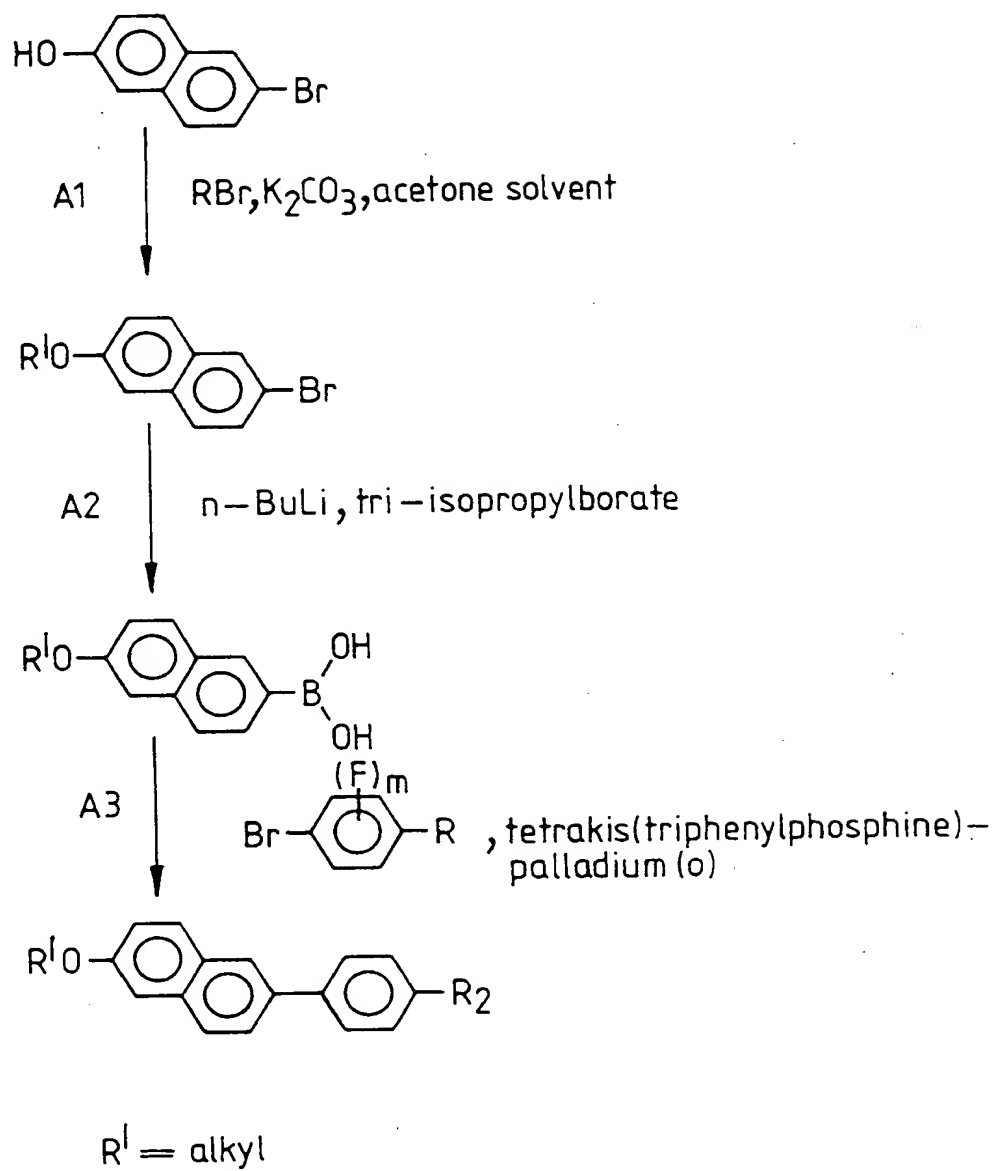
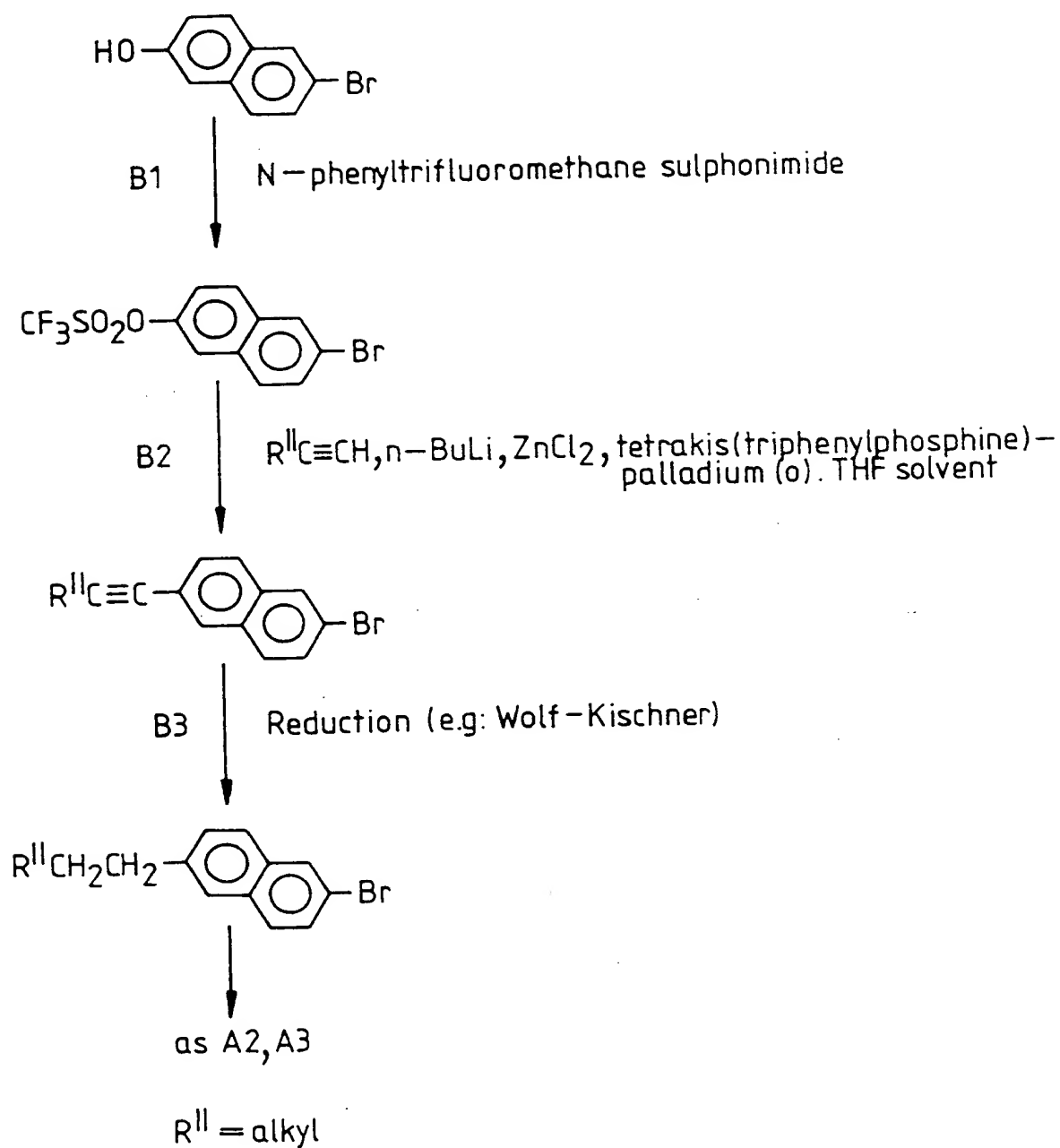
Route A

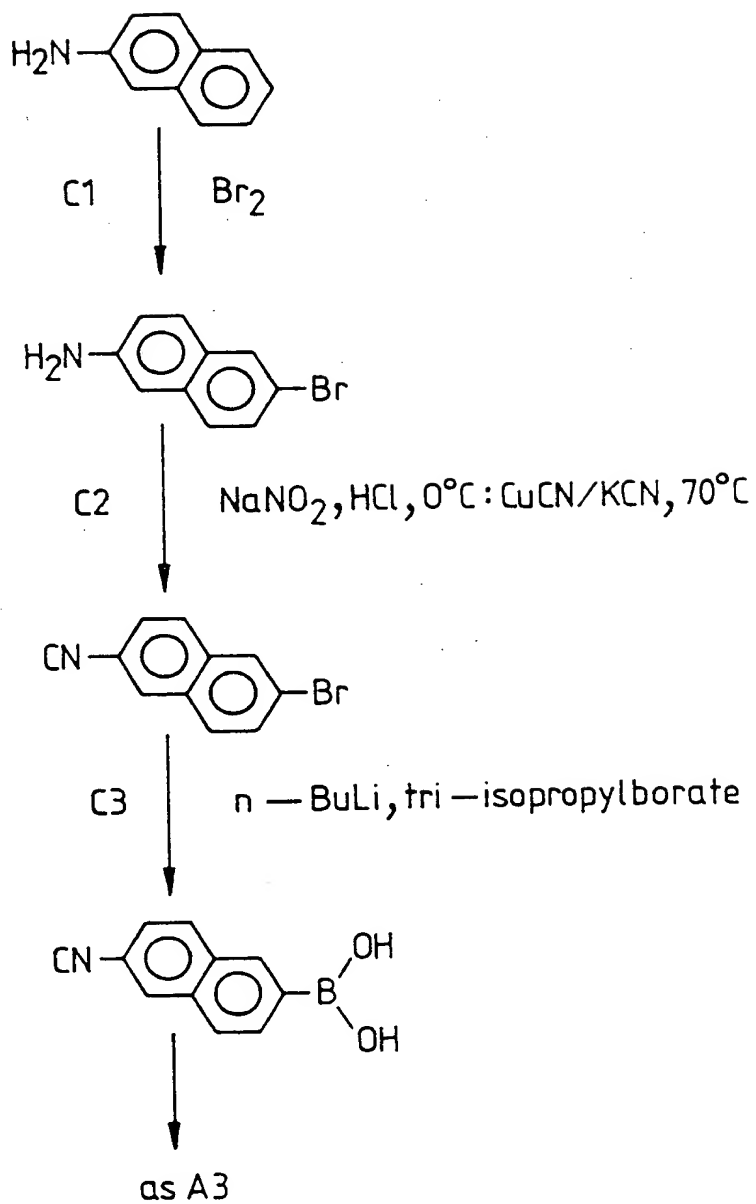
Fig. 2.

Route B

3/4

Fig. 3.

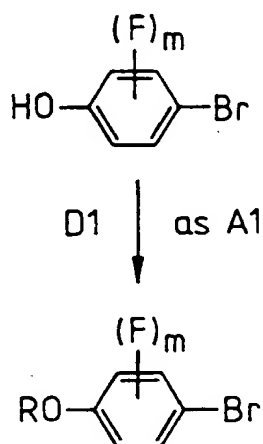
Route C



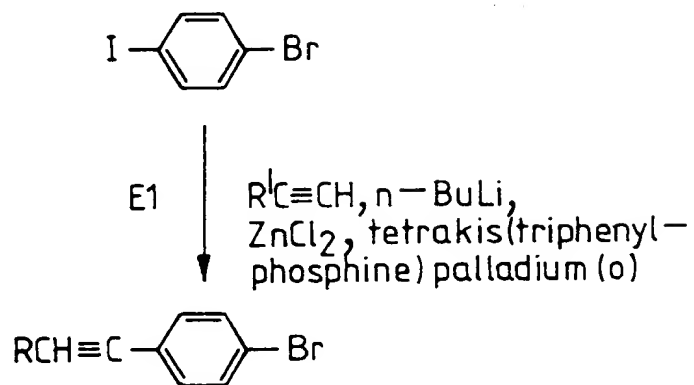
Routes D, E & F

Fig. 4.

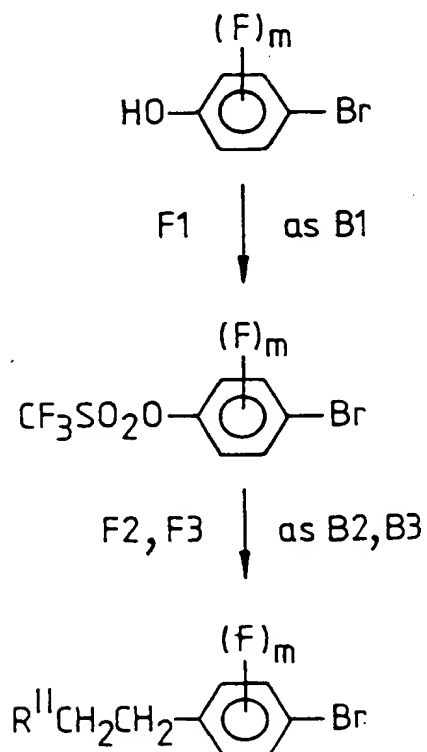
Route D



Route E



Route F



PHENYL-NAPHTHALENES HAVING
LIQUID CRYSTALLINE PROPERTIES

This invention relates to novel phenyl-naphthalenes having liquid crystalline properties and to their use in liquid crystal materials and devices.

Liquid crystal materials and devices exploit the electro-optical properties of nematic or cholesteric (N or N*), or smectic (S) in particular chiral smectic C (Sc*) or smectic A (SA) phases. The most common type of liquid crystal materials in use are those which show a nematic phase, and these are extensively used in for example watches, clocks, calculators, electronic displays etc.

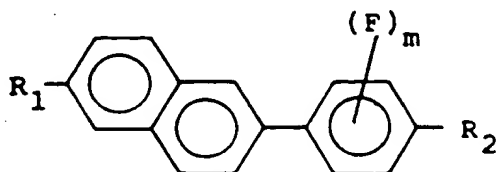
Liquid crystal materials desirably are easy to prepare, show liquid crystal phases which persist over a wide temperature range which preferably includes room temperature, and useful physico-chemical properties such as birefringence. For some applications of liquid crystal materials a high birefringence is sought, e.g. in the so-called "electrically controlled birefringence" (ECB) effect device (see, for example, M F Schieckel and K Fahrenschon Appl. Phys. Lett (1971), 19, 2912), in thin film transistors (TFT) or supertwist twisted

nematic (STN) devices. It is rare for all the requisite desirable properties to be found in a single liquid crystalline compound, and generally liquid crystal materials consist of mixtures of component compounds. Very many liquid crystalline compounds suitable for such uses are known and will be apparent to those skilled in the art.

Some investigations have been carried out of compounds containing a naphthyl group, for example Applicant's co-pending GB 8900871 (Applicant's Ref: P0743) describes a series of such compounds, as components of liquid crystal materials.

It is an object of this invention to provide novel phenyl-naphthalene compounds having liquid crystalline properties or being otherwise suitable for use as component compounds in liquid crystal materials.

According to this invention phenyl-naphthalenes of general formula I are provided :



Formula I

wherein R_1 is C_{1-15} alkyl or alkoxy or perfluoro-alkyl or perfluoro-alkoxy, or CN; R_2 is CN, halogen, C_{1-15} perfluoroalkyl or perfluoroalkoxy, NCS, C_{1-15} alkyl or alkynyl; m is 0, 1 or 2 provided that R_1 and R_2 are not both alkyl, alkoxy, perfluoroalkyl or perfluoroalkoxy unless m is 0.

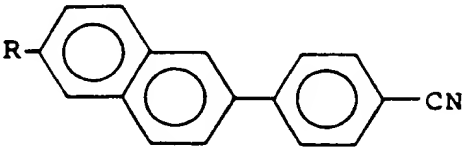
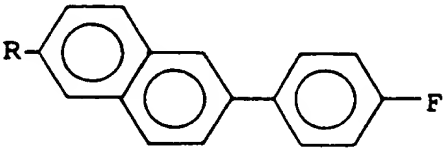
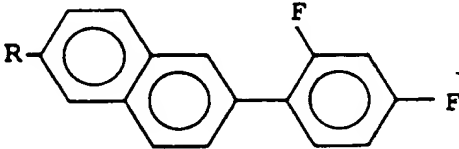
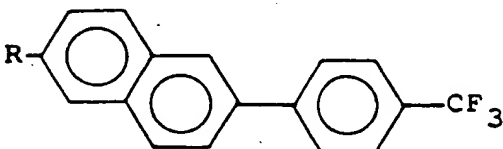
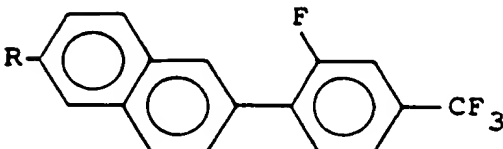
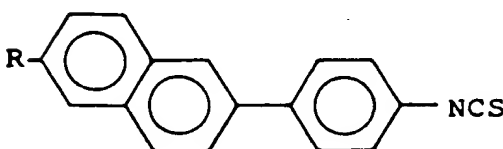
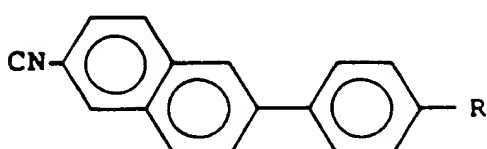
The preferred embodiments of the invention discussed below are inter alia chosen with respect to ease of preparation and their liquid crystal properties, particularly with respect to suitability for use in high birefringence nematic liquid materials.

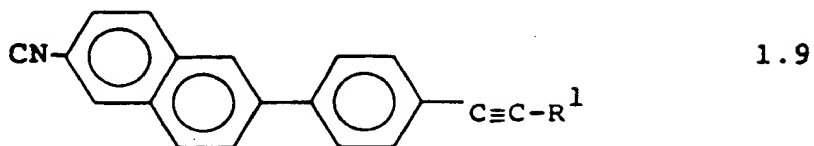
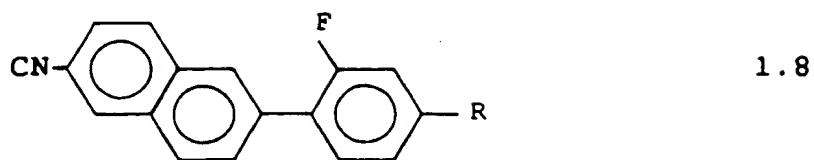
Preferably R_1 and R_2 , if organic substituents, contain 1-8 carbon atoms. A preferred halogen for R_2 is fluorine. A preferred perfluoroalkyl group is CF_3 . When m is 2 the two fluorines are preferably in the 2,3-substitution positions on the phenyl ring.

Preferably one of R_1 and R_2 is a non-polar group, such as alkyl, alkoxy or alkynyl and the other is polar, such as CN, halogen (e.g. fluorine), NCS or a CF_3 -terminated perfluoroalkyl or perfluoroalkoxy such as CF_3 itself.

Preferred overall structures for the phenyl-naphthalenes of formula I are listed below :

Table 1

	1.1
	1.2
	1.3
	1.4
	1.5
	1.6
	1.7



where R is alkyl or alkoxy, especially alkoxy and R¹ is alkyl.

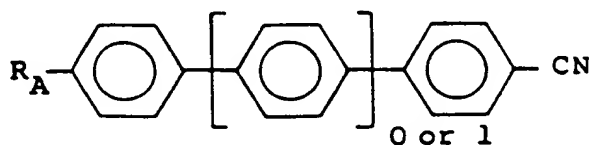
Phenyl-naphthalenes of formula I may be prepared by generally applicable routes shown in Figures 1 to 3 of the accompanying drawings. 2-hydroxy-6-bromonaphthalene and 2-aminonaphthalene are known. In these routes the reaction conditions of the individual steps are well known but the overall combination of steps to form the end product is novel. Compounds in which R₂ is NCS, e.g. 1.6, are preferably prepared by initially incorporating an amino group into the molecule as R₂, for example coupling the boronic acid with para-bromoaniline in step A3, and then converting this into an isothiocyanate. Ways of doing this will be apparent to those skilled in the art.

Routes D, E and F illustrate methods by means of which parabrominated intermediates for use in step A3 may be prepared.

This invention also provides a liquid crystal material being a mixture of at least two component compounds, at least one of which is a phenyl-naphthalene of formula I.

Phenyl-naphthalenes of formula I have nematic liquid crystalline properties. In particular, many have a high birefringence, making them suitable for applications in which this characteristic is required, as discussed above. Although some have rather high melting points, this can be in some cases be usefully reduced by introducing one or more lateral fluoro-substituents on the phenyl ring, e.g. as in 1.3, 1.5 and 1.8.

These compounds may be used as components of liquid crystal materials together with other known liquid crystalline compounds especially for example compounds of general formula II :



Formula II

where R_A is C_{1-10} n-alkyl or n-alkoxy. Other known compounds which may be usefully included as components of liquid crystal materials include those described, for

exampl , in GB-1551043, GB-1556994, GB-1592147,
GB-1587819, GB-1603076, GB-2011940, GB-2023136,
GB-2027708, GB-2027027, GB-2058789, GB-2063250,
GB-2071649, GB-2070594, GB-2071131, GB-2081707,
GB-2079275, GB-2080820, GB-2089345, GB-A-8203798,
EP-0060648, GB-2111974, US-4482472, GB-2118934,
US-4506957, GB-2121406, EP-A-83303348.3, GB-2134110,
EP-A-8430494.3, EP-A-84303240.0.

Generally, phenyl-naphthalenes of this invention may constitute 5-50% by weight of such a liquid crystal material.

Liquid crystal materials of the invention may be used in display devices of known construction and method of operation. Typically, an electrooptical display device will consist of two substrates between which a layer of the liquid crystal material may be sandwiched. At least one of the substrates is optically transparent, and both have electrodes which are preferably made of a transparent material on their opposing faces. By applying an electric field across the layer of liquid crystal material via the electrodes an electrooptic effect is achieved which may be viewed directly or preferably through one or more polarising filters.

The invention will now be described by way of example only with reference to Figures 1 to 4 which show preparation routes to phenyl-naphthalenes of Formula I.

Example 1, Route A

Step A1

A stirred solution of 1-bromobutane (50 g, 0.36 mol) in acetone was added dropwise to a stirred refluxing mixture of 2-hydroxy-6-bromonaphthalene (40 g, 0.18 mol) and potassium carbonate (51 g, 0.37 mol) in acetone (300 ml). The stirred mixture was heated under reflux for 24 hr (i.e. until glc analysis revealed a complete reaction). The potassium carbonate was filtered off, water was added to the filtrate and the product was extracted into ether twice. The combined ethereal extracts were washed with water, 5% sodium hydroxide, water and dried. The solvent and the excess of 1-bromobutane were removed in vacuo. The crude product was recrystallised from ethanol to yield an off-white powder.

Yield 32.3 g (64%) mp 52-53°C.

Step A2

n-Butyllithium (12.4 ml, 2.5 M in hexane, 0.031 mol) was added dropwise to a stirred cooled (-78°C) solution of the product of step A1 (8.602, 0.031 mol) in dry THF (60 ml) under dry nitrogen. The reaction mixture was maintained under these conditions for 1.5 hrs and then a previously cooled solution of tri-isopropyl borate (12.0 g, 0.064 mol) in dry THF (50 ml) was added dropwise at -78°C. Lithiation was monitored by glc analysis. The reaction mixture was allowed to warm to room temperature overnight and then stirred for one hour with 10% hydrochloric acid (30 ml). The product was extracted into ether (twice), and the combined ethereal extracts were washed with water and dried (MgSO_4). The solvent was removed in vacuo to yield a colourless solid.

Yield 8.5 g (100%)

Step A3

A solution of para-bromobenzonitrile (1.25 g, 6.87 mmol) in ethanol (15 ml) was added to a stirred mixture of the product of step A2 (2.01 g, 8.24 mmol) and tetrakis-(triphenyl phosphine) palladium (0) (0.2917 g, 0.25 mmol) in benz n (30 ml) and 2M sodium carbonat

(30 ml) at room temperature under dry nitrogen. The stirred mixture was heated under reflux ($\sim 100^{\circ}\text{C}$) for 4 hrs (i.e. until glc and tlc analysis revealed a complete reaction). The product was extracted into ether (twice) and the combined ethereal extracts were washed with brine and dried (MgSO_4). The solvent was removed in vacuo and the residue was purified by column chromatography [silica gel/petroleum fraction (bp $40-60^{\circ}\text{C}$) - dichloromethane, 3:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (8:1) to yield colourless crystals.

Yield 1.63 g (79%).

Example 2, Route E

A solution of n-butyllithium (7.8 ml, 10.0 M in hexane, 0.078 mol) was added dropwise to a stirred, cooled (-5 to 0°C) solution of pent-1-yne (5.28 g, 0.078 mol) in dry THF (50 ml) under dry nitrogen. This mixture was stirred for 10 min and then a solution of dry zinc chloride (10.80 g, 0.079 mol) in dry THF (100 ml) was added dropwise at -5 to 10°C . The mixture was stirred at room temperature for 15 min and a solution of para-iodobromobenzene (5.28 g, 0.078 mol) in dry THF (100 ml) was added dropwise at -5 to 0°C followed by the addition of tetrakis (triphenylphosphine)palladium (0)

(2.80 g, 2.40 mmol). The mixture was stirred at room temperature overnight (glc analysis revealed a complete reaction) and poured into 10% hydrochloric acid. The product was extracted into ether (twice) and the combined ethereal extracts were washed with aqueous sodium hydrogen carbonate and dried (MgSO_4). The solvent was removed in vacuo to afford a liquid which was filtered through a short alumina column and eluted with dichloromethane. The solvent was removed in vacuo and the residue distilled to yield an oil.

Yield 14.20 g (82%) bp 130-134°C at 15 mm Hg.

Example 3, Steps B1 and B2

B1 A solution of N-phenyltriflamide (4.93 g, 0.0138 mol) in dry dichloromethane (50 ml) was added dropwise to a stirred cooled (-78°C) solution of 2-hydroxy-6-bromonaphthalene (2.80 g, 0.0126 mol) in dry dichloromethane (80 ml) and dry triethylamine (2.55 g, 0.25 mol) under dry nitrogen. The stirred mixture was allowed to warm to room temperature overnight (glc and tlc analysis revealed a complete reaction). The mixture was washed with aqueous sodium carbonate and the separated aqueous layer was washed with dichloromethane. The combined organic extracts were washed with water and dried (MgSO_4). The solvent was removed in vacuo and

th residue was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid.

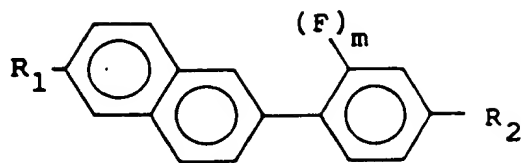
Yield 4.40 g (98%) mp 52-53°C.

B2 Quantities: pent-1-yne (0.48 g, 7.14 mmol), n-butyllithium (2.90 ml, 2.5M in hexane, 7.25 mmol), zinc chloride (1.00 g, 7.35 mmol), the product of step B1 (2.14 g, 6.64 mmol), tetrakis(triphenylphosphine) palladium (0) (0.2621 g, 0.23 mmol), lithium chloride (0.5812 g, 14 mmol).

The experimental procedure was similar to that of route E described above, except that lithium chloride was added with the tetrakis (triphenylphosphine)palladium (0) and the mixture was heated under reflux (oil bath at 100°C) for 22 hours (overnight for convenience; glc and tlc revealed a complete reaction). The crude product was purified by column chromatography (silica gel/petroleum fraction (bp 40-60°C) - dichloromethane, 10:1) to give a colourless solid which was recrystallised from ethanol - ethyl acetate (3:1).

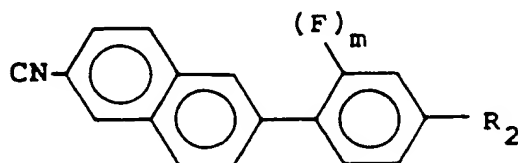
The properties of the compound prepared in the examples above and of others prepared by analogous routes using different R₂ groups are listed below (K = solid crystal).

Table 2



R_1	R_2	m	<u>Liquid Crystal Transitions ($^{\circ}\text{C}$)</u>		
$\text{C}_4\text{H}_9\text{O}$	CN	0	K 125.0	N 156.5	I
$\text{C}_4\text{H}_9\text{O}$	F	0	K 128.5	(N 112.9)	I
$\text{C}_4\text{H}_9\text{O}$	F	1	K 72.0	(N 63.0)	I
$\text{C}_4\text{H}_9\text{O}$	CF_3	0	K 177.5	(N 95.0)	I
$\text{C}_4\text{H}_9\text{O}$	CF_3	1	K 73.5	S_A 105.5	I

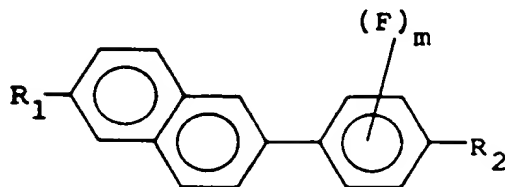
Table 3



R_2	m	<u>Liquid Crystal Transitions ($^{\circ}\text{C}$)</u>		
OC_4H_9	0	K 98.5	167.5	I
OC_4H_9	1	K 64.5	N 129.5	I
$\text{C}\equiv\text{C}_3\text{H}_7$	0	K 113.0	N 193.0	I

CLAIMS

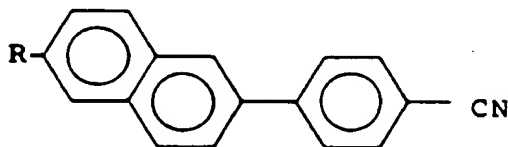
1. Phenyl-naphthalenes of general formula I :



Formula I

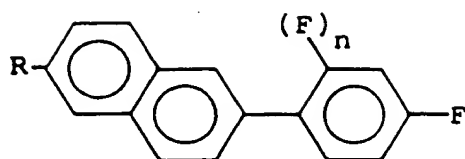
wherein R_1 is C_{1-15} alkyl or alkoxy or perfluoro-alkyl or perfluoro-alkoxy, or CN; R_2 is CN, halogen, C_{1-15} perfluoroalkyl or perfluoroalkoxy, NCS, C_{1-15} alkyl or alkynyl; m is 0, 1 or 2 provided that R_1 and R_2 are not both alkyl, alkoxy, perfluoroalkyl or perfluoroalkoxy unless m is 0.

2. Phenyl-naphthalenes according to claim 1, having an overall structure :



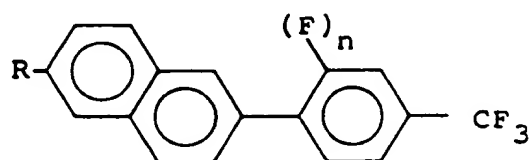
wherein R is alkyl or alkoxy.

3. Phenyl-naphthalenes according to claim 1, having an overall structure :



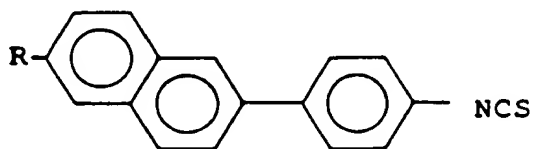
wherein R is alkyl or alkoxy and n is 0 or 1.

4. Phenyl-naphthalenes according to claim 1, having an overall structure :



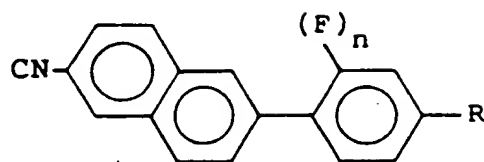
wherein R is alkyl or alkoxy and n is 0 or 1.

5. Phenyl-naphthalenes according to claim 1, having an overall structure :



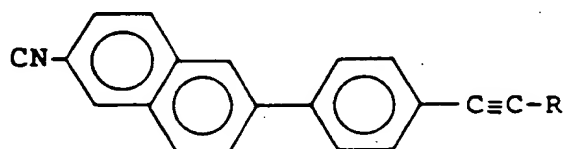
wherein R is alkyl or alkoxy.

6. Phenyl-naphthalenes according to claim 1, having an overall structure :



wherein R is alkyl or alkoxy and n is 0 or 1.

7. Phenyl-naphthalenes according to claim 1, having an overall structure :



wherein R is alkyl.